Synergistic insecticidal compositions containing essential oils of citrus fruit peel and an alkanoic acid

Patent Number:
Publication date: 1996-06-18
Inventor(s):
Applicant(s):: OFER YAACOV (IL)
Requested Patent: IL105109
Application Number: IL19930105109 19930318
Priority Number(s): IL19930105109 19930318
IPC Classification: A01N65/00
EC Classification:
Equivalents:

Abstract

CIT. BIOFLAV

Background Explanation: Bioflavonoids occur in flowers, fruits, vegetables, seeds, leaves, nuts and bark.

Bioflavonoids

Hesperidin

Hesperidin is one of the bioflavinoids, naturally occurring nutrients usually found in association with Vitamin C. Some symptoms originally thought to be due to Vitamin C deficiency such as bruising due to capillary fragility were found in early studies to be relieved by crude vitamin C extract but not by purified Vitamin C. The bioflavinoids, sometimes called Vitamin P, were found to be the essential component in correcting this bruising tendency and improving the permeability and integrity of the capillary lining. These bioflavinoids include Hesperidin, Citrin, Rutin, Flavones, Flavonals, Calechin, and Quercetin.

Hesperidin deficiency has been linked with abnormal capillary leakiness as well as pain in the extremeities causing achiness, weakness, and night leg cramps. Supplemental Hesperidin may also help reduce edema or excess swelling in the legs due to fluid accumulation. Like other bioflavinoids, hesperidin works best when given with Vitamin C and other bioflavinoids. No signs of toxicity have been observed with normal intake. (Smart Basics)

Lemon

By definition, Bioflavonoids are any of a group of colored substances found in many fruits, and essential for the absorption and processing of vitamin-C. These substances are not vitamins, per se, but, were dubbed "vitamin P" by Dr. Albert Szent-Gyorgyi, a famed Hungarian researcher. He is one and the same Gyorgyi who won the Nobel Prize in Medicine for his discovery of vitamin C. It was in the course of isolating vitamin C that he came across the Bioflavonoids. He had a friend with bleeding gums and thought this condition might have something to do with a vitamin C deficiency. He gave the man some of his raw , impure vitamin C, and sure enough the bleeding gums cleared up.

Later on, confronted by a recurrence of bleeding gums, he decided to try again; this time with pure vitamin C, he expected to observe an even more dramatic result. No such luck. The man's gums went right on bleeding. Szent-Gyorgi re-examined his earlier preparation and decided that the effective impurity was one of the Bioflavonoids. He then tried these by themselves, and reported that they worked. He named these substances "vitamin P." The Bioflavonoids thus first came into use as primarily as protectors of capillaries, the tiniest blood vessels in the body.

Until 1968, many doctors were prescribing Bioflavonoids . Then in 1968, the FDA, relying on a review of literature conducted by a panel of the National Academy of Sciences/National Research Council, withdrew the bioflavonoid drugs from the marketplace, declaring that they were ineffective in humans "for any condition". That FDA directive stopped physicians from prescribing Bioflavonoids, But did nothing to prevent consumers from purchasing them in health-food stores, usually in combination with vitamin C.

Now we are seeing a true resurgence in interest in the Bioflavonoids. An abstract of a review article in the publication, "Trends in Pharmacological Sciences" says..."Naturally occurring flavonoids have potent anti-allergy , inti-inflammatory and anti-viral activity. Since they are common dietary constituents, the question arises: are they natural biological response modifiers?" What has happened in that despite all the controversy, there were always a few scientists who kept on studying the flavonoids. (Vitawise)

Rutin

"... Rutin is a nonmutagenic flavonol glycoside, whereas its aglycone quercetin is mutagenic. Cell-free preparations from fecal cultures (fecal preparations) contain a beta-glucosidase that, when incubated with rutin, hydrolyzes it to quercetin.

This activity can be further induced when rutin is added to the fecal culture from which the cell-free preparation is made.

When vitamin pills that contain rutin are added to the cultures, this induction is equally effective. The vitamin extracts by themselves, like rutin, were nonmutagenic; however, when the vitamin extracts were incubated with fecal preparations containing induced beta-glucosidase, a great increase in mutagenicity was observed..." (Appl Environ Microbiol)

"Rutin partially protected oxy-Hb against H2O2-induced oxidation and heme loss. Rutin was also shown to delay H2O2-induced met-Hb oxidation to ferryl-Hb. Rutin directly reduced ferryl-Hb to oxy-Hb in stoichiometric (1:1) reaction characterized by a rate constant of 100 to 130/M/sec. It is assumed that by reducing ferryl-Hb, rutin prevents oxy-Hb from reacting with ferryl-Hb (comproportionation reaction), thus preventing half of the oxy-Hb molecules from being converted to met-Hb. This mechanism is consistent with 50% inhibition by rutin (at the maximum of its activity) of PQ-induced oxy-Hb oxidation in RBC. The present results demonstrate new antioxidant properties of rutin that may be useful in diminishing oxidative damage to pathological red blood cells..." (Biochem Pharmacol)

Quercitin

Bioflavonoids are nutrients which are related to the vitamin C family. They cannot be synthesized by the body, and therefore must be obtained from foods or supplements. At the Second International Conference on Antiviral Research, it was reported that the bioflavonoid quercetin, when combined with Vitamin C, showed anti viral activity against organisms that cause colds. Bioflavonoids are also helpful in nourishing the integrity and strength of capillaries and cells. (Enrich)

חוק הפטנטים, התשכ"ז–1967
PATENTS LAW, 5727–1967

בקשה לפטנט
Application for Patent

לשימוש הלשכה
For Office Use

מספר: Number	105109/3
תאריך: Date	18 - 03 - 1993
הוקדם/נדחה Ante/Post-dated	

אני, (שם המבקש, מענו – ולגבי גוף מאוגד – מקום התאגדותו)
I (Name and address of applicant, and, in case of body corporate-place of incorporation)

דייר יעקב עופר
רחוב הפועל 11
נוף-ים
הרצליה 46626

DR YAACOV OFER
REHOV HAPOEL 11
NOF-YAM
HERZLYA 46626

בעל אמצאה מכח _____
Owner, by virtue of

ששמה הוא _____
of an invention, the title of which is

(בעברית)
(Hebrew)
תכשירים סינרגיסטיים קוטלי חרקים המכילים שמנים ריחניים של קליפות פרי הדר וחומצה אלקאנוית

(באנגלית)
(English)
SYNERGISTIC INSECTICIDAL COMPOSITIONS CONTAINING ESSENTIAL OILS OF CITRUS FRUIT PEEL AND AN ALKANOIC ACID

מבקש בזאת כי ינתן לי עליה פטנט
hereby apply for a patent to be granted to me in respect thereof.

• בקשת תלוקה – Application of Division	• בקשת פטנט מוסף – Application for Patent Addition	• דרישה דין קדימה Priority Claim		
מבקשת פטנט from Application	• לבקשה/לפטנט to Patent/Appl.	מספר/סימן Number/Mark	תאריך Date	מדינת האגוד Convention Country
No. _____ מס'	No. _____ מס'			
dated _____ מיום	dated _____ מיום			

• יפוי כח: כללי/מיוחד – רצוף בזה / עוד יוגש
P.O.A.: general / individual – attached / to be filed later –

הוגש בענין _____
Filed in case

המען למסירת הודעות ומסמכים בישראל
Address for Service in Israel
דייר יעקב עופר,
רחוב הפועל 11, נוף-ים
הרצליה 46626.

חתימת המבקש
Signature of Applicant

היום _____ בחודש _____ שנת _____
This _____ day of _____ of the year

לשימוש הלשכה
For Office Use

תאריך הפרסום: 19-09-1996
Publication date:
תאריך מחיתום:

SYNERGISTIC INSECTICIDAL COMPOSITIONS CONTAINING ESSENTIAL OILS OF CITRUS FRUIT PEEL AND AN ALKANOIC ACID

תכשירים סינרגיסטיים קוטלי חרקים המכילים שמנים ריחניים של קליפות פרי הדר וחומצה אלקאנוית

105109/2

The present invention relates to synergistic insecticidal compositions; more particularly to synergistic compositions containing as active ingredients capric acid and an essential oil and their use as effective insecticides,larvicides and ovicides to the order hymenoptera and in particular the family formicidae[ants]. Most preferred synergistic compositions containing as active ingredients capric acid and an essential oil selected from orange,lemon and grapefruit and mixtures of said essential oils. It was surprisingly found that such synergistic compositions showed a lethal effect on ants. The said synergistic compositions are inexpensive to produce and imparts a pleasant aroma.

BACKGROUND OF THE INVENTION.

Ant infestation in many countries such as the USA and Israel has become a serious problem in domestic residences,kitchens,food stores, restaurants and hospitals.There are number of commercial insecticides such as for example, allethrin, pyrethrum, malathion, piperonyl butoxide, methoxychlor,carbaryl and the like have been used in the control of ants.

It has been disclosed that essential oils have pesticidal activity. Su et al [J. Agric.Food Chem., 35,509, 1987.] discloses that lemon peel oil is insecticidally active to cowpea weevils and rice weevils. Abbassy et al [Meded. Fac. Landbouwwet., Rijksuniv. Gent.44, 21,1979.] demonstrated the insecticidal and synergistic properties of lemon peel oil to flour beetles and granary weevils.

l-menthol has been used for controlling beetles, termites and ants [Ishidi et al; Jpn Kokai Tokkyo Koho JP 03,141,201(17 -6-1991)].

Ahmed et al [Indian Perfum. 30(1), 273 (1986)] evaluated essential oils for their vapour toxicity to houseflies and to stored-product insect pests such as weevils and beetles. Chavan et al; [Bull.Hafkine Inst., 11(1), 18 (1983).] showed that certain essential oils of *Ocimum santum*, *O.basilicum* and *Eucalyptus globulus* or mixtures thereof were active on mosquito larvae.

Insecticidal formulations selected from organophosphates, carbamates.pyrethroids and triazines were used in the control of ants in soils. [Japan Kokai Tokyo Koho JP 64 00,003.]

Guarana essential oil in a mixture containing dipterex,sugar,flour, kaolin,salicylic acid,rhodamin and CMC was used as an ant-killing paste.[Braz.Pedido PI BR 87 04,465.]

Aerosol formulations containing pyrethrum extract and citral or citronellal as attractants were used for the control of ants.

[French Demande FR 2,477,375 (11 Sept.1981)].

It has been disclosed by McFarlane & Henberry [Comp. Biochem. Physiol., 24, 377 (1968)] that C_{12} fatty acids, among others, inhibit the growth of crickets. C_8-C_{11} Fatty acids such as undecanoic acid, are effective insecticides to beetles, *Calandra oryzae* [Ikan et al, Israel J. Entomology, XI, 81, (1976)].

These fatty acids are found to be useful for protecting stored products,such as wheat, as they are effective insecticides to certain beetles [Ikan & Shaaya,Israel Patent No.53570].
These fatty acids also act as effective larvicides to the housefly (*Musca domestica*) {Quraishi & Thorsteinson, J. Econ. Entomol., 58, 400 (1965)}.
It has been disclosed that octanoic acid has ovicidal activity to the eggs of *Aedea aegypti*. {J.Econ. Entomol., 103, 1435, (1971)}. Crammer et al has shown that C_8-C_{12} fatty acids were effective as licides to lice and lice eggs. [US Patent No. 5,064,859 corresponding to Israel Patent No. 81350].

There is no mention in the above prior art of synergistic compositions containing fatty acids and essential oils for the control of ants.

SUMMARY OF THE INVENTION.

Surprisingly synergistic compositions contain as active ingredients fatty acids of the formula RCOOH wherein R is a C_9-C_{11} straight or branched alkyl group and an essential oil or mixtures thereof derived from the citrus fruit peel were found to be highly effective in the control of insects of the order hymenoptera and in particular in the control of ants, larvae and eggs of the family Formicidae.Furthermore the fatty acids such as capric acid and undecanoic acid are not only very stable but are the least toxic compared to the commercially available insecticides used in the control of ants.The essential oils of citrus fruit peels derived from orange, lemon and grapefruit or mixtures thereof are also stable, non toxic and inexpensive to produce.

Solid or liquid baits suitable for controlling ants comprise the synergistic composition of the fatty acid and essential oil or mixtures thereof and a carrier or diluent which may include a food substance or some other substance to induce consumption by the ants.

It was found that only 0.1% to 5.0% by weight of the essential oil or a mixture of said oils and 0.25% to 1.0% by weight of the fatty acid as defined above gave excellent results for the control of adult ants, and their larvae and eggs.

Preferred synergistic compositions according to the invention are those in which the moiety R of the fatty acid of the formula RCOOH is nonyl and the essential oil or a mixture thereof is selected from the citrus fruit peel of orange, lemon and grapefruit.

Particularly preferred synergistic compositions are those in which the carboxylic acid is capric acid and the essential oil is orange, lemon or grapefruit or a mixture thereof. The synergistic composition of the invention contains 0.1% to 5.0% by weight of the essential oil or mixture thereof and 0.25% to 1.0% by weight of the carboxylic acid.For example a synergistic composition may contain 0.25% capric acid and 1.0% orange oil.

The invention further provides a method of controlling ants and their larvae and eggs, in particular,*Tapinoma simrothi* and *Polyrhachis simplex* which comprises applying an effective quantity of the synergistic composition as defined above to the ants and their larvae.

The synergistic compositions of the invention are soluble in organic solvents making liquid formulations very simple and easy to handle.

The synergistic compositions containing the active ingredients selected from a fatty acid and an essential oil as defined above can be converted to the customary formulations, such as solutions, emulsions, wettable powders, suspensions, powders, granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with the active synergistic composition.

These formulations are produced in a known manner, for example by mixing the synergistic composition with extenders, that isliquid solvents and/or solid carriers, optionally with the use of surface-active agents, that is emulsifying agents and/or dispersing agents and/or foam forming agents.In the usof water as an extender, organic solvents can, for example, be used as auxiliary solvents.

As liquid solvents, there are suitable in principle, aromatics such as xylene, toluene or alkyl naphthalenes;chlorinated aromatics and chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride; aliphatic and cycloaliphatic hydrocarbons, such as hexane, heptane and cyclohexane; paraffins, for example, petroleum fractions; mineral and vegetable oils; alcohols such as ethanol,isopropanol or glycol as well as their ethers and esters; ketones, for example, acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone; strongly polar solvents, such as dimethylformamide and dimethylsulphoxide as well as water.

Suitable solid carriers include natural and synthetic clays and silicates, for example, natural silicates such as diatomaceous earths; magnesium silicates, for example talcs; magnesium aluminum silicates,for example attapulgites and vermiculites;aluminum silicates, for example kaolinites, montmorillonites and micas; calcium carbonate; calcium sulphate; synthetic hydrated silicon oxides and synthetic calcium or aluminum silicates; coumarone resins, polyvinyl chloride and styrene polymers and copolymers.

The synergistic compositions of the invention may, for example, be formulated as wettable powders, dusts, granules, solutions, emulsifiable concentrates, emulsions, suspension concentrates and aerosols.
Wettable powders may contain up to 15% by weight of active ingredients and usually contain, in addition to solid inert carriers, 3-10% by weight of a dispersing agent and, if desired, up to 10% by weight of a stabilizer and/or other additives such as penetrants or stickers.

The wettable or soluble powders containing the active ingredients may be used to treat substrates or sites infested or liable to infestation by ants including premises, outdoor or indoor storage or processing areas, containers or equipment and standing or running water.
Dusts are usually formulated as dust concentrates having similar compositions to that of wettable powders but without a dispersant and are diluted, prior to use with a further solid carrier to yield compositions usually containing up to 75% by weight of active ingredients.
Granules are prepared to have a size between 10 and 100 BS mesh [1.67 - 0.15 mm], and may be manufactured by agglomeration or impregnation techniques. Usually, granules will contain up to 25% by weight of active ingredients and 0.10% by weight of additives such as stabilizers, slow release modifiers and binding agents.

Emulsifiable concentrates often contain,in addition to an organic solvent such as xylene, mixtures of various emulsifying and wetting agents,whereby the resulting concentrate, on dilution with water,forms an emulsion of the active synergistic mixture in water. There may be used 10 - 50% w/v active ingredients, 2 - 20% w/v emulsifiers and up to 20% w/v of other additives including stabilizers such as polyvinyl alcohol, penetrants and corrosion inhibitors.

Suspension concentrates are usually compounded so as to obtain a stable non-sedimenting flowable product and contains 5 - 80% by weight of active ingredients, 0.5 - 15% by weight of dispersing agents, 0.1 - 10% by weight of suspending agents such as protective colloids and thixotropic agents, up to 10% by weight of other

additives such as defoamers, corrosion inhibitors, stabilizers, penetrants, stickers and water or an organic liquid in which the active ingredients is substantially insoluble; certain organic solids or inorganic salts may be present dissolved in the formulation to assist in preventing sedimentation or as anti-freeze agents for water.
The synergistic compositions in the form of aerosols and aqueous or non-aqueous solutions or dispersions suitable for spraying, fogging and low- or ultra-low volume spraying may also be used.

BRIEF DESCRIPTION OF THE FIGURES.

Figure 1 is a bar graph representing the results according to example 1 illustrating the insecticidal activity [% mortality] of the concentration of capric acid in methylene chloride on ants {*Tapinoma simrothi*}.

Figure 2 is a bar graph representing the results according to example 2 illustrating the insecticidal activity [% mortality] of the concentration of lemon oil in methylene chloride on ants {*Tapinoma simrothi*}.

Figure 3 is a bar graph representing the results according to example 3 illustrating the synergistic insecticidal activity [% mortality] of the concentration of different essential oils and capric acid in methylene chloride on ants {*Tapinoma simrothi*}.

Figure 4 is a bar graph representing the results according to example 4 illustrating the synergistic insecticidal activity [% mortality] of different concentrations of lemon oil, capric acid and a synergistic mixture of the two compounds in methylene chloride on the eggs and larvae of ants {*Polyrhachis simplex*}.

The formulations of the essential oils and capric acid in Figure 3 are as follows:

A = 0.25% Capric acid + 1.0% Orange oil.
B = 0.50% Capric acid + 0.5% Orange oil.
C = 0.25% Capric acid + 1.0% Lemon oil.
D = 0.50% Capric acid + 0.5% Lemon oil.
E = 1.00% Capric acid + 1.0% Lemon oil.
F = 0.50% Capric acid + 0.5% Grapefruit oil.
G = 0.25% Capric acid + 1.0% Grapefruit oil.
H = 0.25% Capric acid + 1.0% Orange oil + 1.0% Lemon oil.
I = 0.25% Capric acid + 1.0% Lemon oil + 1.0% Grapefruit oil + 1.0% Orange oil.
J = 0.50% Capric acid + 0.5% Lemon oil + 0.5% Orange oil +0.5% Grapefruit oil.

The formulations of lemon oil and capric acid in Figure 4 are as follows:

3% Lemon oil [L.O.]
5% Lemon oil [L.O.]
7% Lemon oil [L.O.]
0.25% Capric acid [C.A.]
0.50% Capric acid [C.A.]
1% Capric acid [C.A.]
2 % Capric acid [C.A.]
0.25% Capric acid + 3% Lemon oil [Synergistic mixture].

The invention will now be described in more detail in the following non-limiting examples and,where applicable, their accompanying figures.

The results described and illustrated herein by way of non-limiting examples were obtained by applying the liquid formulations of the present invention to ants, their eggs and larvae {*Tapinoma simrothi* and *Polyrhachis simplex*}. These formulations contain as active ingedients a carboxylic acid of the formula R-COOH wherein R is a C_9 - C_{11} straight or branched alkyl group and an essential oil of the citrus fruit peel or a mixture of the citrus fruit as hereinbefore defined and as exemplified hereinbelow by capric acid and the essential oil of peels of citrus fruit selected from orange, lemon and grapefruit or mixtures thereof. It is to be understood therefore that the exemplified formulations, their component synergistic active ingredients of capric acid and the essential oil of orange, lemon and grapefruit and method for the control of ants, larvae or eggs of the species *Tapinoma sothimri* and *Polyrhachis simplex* are only preferred embodiments of the present invention. Many other modifications and applications of the present invention will be apparent, for example, the formulations of the present invention may be applied to other species of ants such as, for example, *Monomorium minimum*, *Crematogaster jehovae* and *Pheidole pallidulla*.

FORMULATIONS FOR THE CONTROL OF ANTS.

The following solutions in methylene chloride were prepared:
Example 1.

(a) 0.1%, (b) 0.25%, (c) 0.5%, (d) 1.0%, (e) 2.0%, (f) 3.0% and 5.0% of capric acid.

Example 2.

(a) 1-3% , (b) 5.0% , (c) 7.0%, (d) 13.0% and 15.0% of Lemon oil.

Example 3.

(a) 0.25% Capric acid + 1.0% Lemon oil.
(b) 0.50% Capric acid + 0.5 % Lemon oil.
(c) 0.25 % Capric acid + 1.0 % Lemon oil.
(d) 0.50% Capric acid + 0.5% Lemon oil.
(e) 1.0% Capric acid + 1.0% Lemon oil.
(f) 0.50% Capric acid + 0.5% Grapefruit oil.(gg)
(g) 0.25% Capric acid +1.0% Grapefruit oil.
(h) 0.25% Capric acid + 1.0% Orange oil + 1.0% Lemon oil.
(i) 0.25% Capric acid + 1.0% lemon oil + 1.0% Grapefruit oil + 1.0% Orange oil.
(j) 0.05% Capric acid + 0.5% Lemon oil + 0.5% Orange oil + 0.5% Grapefruit oil.

Example 4.

(a) 3% Lemon oil.
(b) 5% Lemon oil.
(c) 7% Lemon oil.
(d) 0.25% Capric acid.
(e) 0.50% Capric acid.
(f) 1.0% Capric acid.
(g) 2.0% Capric acid.
(h) 3% Lemon oil + 0.25% Capric acid.

TEST METHOD.

[I]

Ten specimens of ants {*Tapinoma simrothi*} were placed on 10 - 15 cm squares of filter paper.The formulation containing one of the active ingredients was sprayed cautiously on the filter paper.The ants were left in contact with the active ingredients for 5 to 10 minutes. Each experiment was repeated three times and for each test a control test was carried out using ten ants.The number of ants surviving were counted.

[II]

A known number of eggs and larvae of the Weaver ant {*Polyrhachis simplex*} were placed together in petri dishes containing circles of filter paper.This was followed by spraying with the solutions enumerated in example 4.

After 15 minutes the p[redacted] dishes were placed in the original ant colony. The response of the ant workers of the colony to the treated eggs and larvae was observed.
The results of these observations are summarized in figure iv.It should be mentioned that the ant workers usually take care of the living eggs and larvae. Every test was repeated four times. The mortality rate of the eggs and larvae was obtained by taking the total number of the eggs and larvae and dividing this number by the number of those eggs and larvae that died during the 15 minutes.

In the following test results will be given to the annexed bar graphs in which:-

FIGURE 1 illustrates the insecticidal activity to ants {*Tapinoma simrothi*} of different concentrations of capric acid in dichloromethane.

FIGURE 2 illustrates the insecticidal activity to ants {*Tapinoma simrothi*} of different concentrations of lemon oil in dichloromethane.

FIGURE 3 illustrates the insecticidal activity to ants {*Tapinoma simrothi*} of different concentrations of synergistic mixtures of capric acid and essential oils and mixtures thereof selected from lemon oil, orange oil and grapefruit oil.

FIGURE 4 illustrates the insecticidal activity of the eggs and larvae of ants {*Polyrhachis simplex*} of lemon oil,capric acid and a mixture of the two showing synergistic activity of the mixture.

RESULTS.

It can be seen that a minimum concentration of 5% capric acid or a concentration greater than 15% of lemon oil are required to produce a near 100% mortality rate. A mixture of 1.0% capric acid and 1.0% lemon oil or a mixture of 0.5% capric acid and a 0.5% mixture of lemon oil, orange oil and grapefruit oil produced a 100% mortality rate of the ants. The results illustrated in Figures 3 and 4 clearly shows synergism using a mixture of capric acid and an essential oil or a mixture thereof.

For further illustration there now follow examples of formulations according to the invention. The formulations are prepared by conventional procedures known to those skilled in the art.

Example 5.
[Throughout, percentages are by weight]

Emulsifiable concentrates.

	(a)	(b)
A mixture according to formulation 3(i)	10%	25%
Calcium dodecylbenzene sulphonate		10%
Castor oil polyethylene glycol ether (36 mol of ethylene oxide)	25%	25%
Cyclohexanone	-	40%
Butanol	15%	-
Xylene mixture	50%	-

Emulsions of any required concentration can be produced from such concentrates by dilution with water.

Example 6.

Solutions.

	(a)	(b)
A mixture according to formulation 3(j)	10%	5%
Polyethylene glycol 400	70%	-
N-methyl-2-pyrrolidone	20%	20%
Epoxidised coconut oil	-	1%
Pétroleum distillate (boiling range 160 - 190° C)	-	74 %

These solutions are suitable for application in the form of micro drops.

Example 7.

Granulates.

	(a)	(b)
A mixture according to formulation 3(h)	5%	10%
Kaolin	94%	-
Highly dispersed silicic acid	1%	-
Attapulgite	-	90%

Example 8.

Coated granulates.

A mixture according to formulation 3(h)	3%
Polyethylene glycol 200	3%
Kaolin	94%

The finely ground active ingredients moistened with polyethylene glycol is uniformly applied in a mixture, to the kaolin moistened with polyethylene glycol. Non-dusty coated granulates are obtained in this manner.

Example 9.

Wettable powders.

	(a)	(b)
A mixture according to formulation 3(h)	10%	15%
Sodium lignosulphonate	7%	5%
Sodium lauryl sulphate	5%	-
Sodium diisobutylnaphthalene sulphonate	-	10 %
Octylphenol polyethylene glycol ether (7-8 mol of ethylene oxide)	-	5%
Highly dispersed silicic acid	8%	15%
Kaolin	70%	50%

The active ingredients are thoroughly mixed with the adjuvants and the mixture is thoroughly ground in a suitable mill, affording wettable powders which can be diluted with water to give suspensions of the desired concentration.

Example 10.

Suspension concentrate.

A mixture according to formulation 3(j)	40%
Ethylene glycol	10 %
Nonylphenol polyethylene glycol (15 mol of ethylene oxide)	6%
Sodium lignosulphonate	10%
Carboxymethylcellulose	1%
37 % Aqueous formaldehyde solution	0.2 %
Silicone oil in the form of a 75% aqueous emulsion	0.8%
Water	32%

The finely ground active ingredients are intimately mixed with the adjuvants,giving a suspension concentrate from which suspensions of any desired concentration can be obtained by dilution with water.

Example 11.

Aerosol.

	%/Wt.
Mixture of active ingredients according to formulation 3(h)	0.5%
Freon 12	99.5%

Preparation: The components are mixed and packaged under pressure in a suitable container equipped with a release spray valve.

WHAT IS CLAIMED IS:

1. Synergisitic composition for the control of insects, their larvae and eggs of the order hymenoptera containing as active ingredients an essential oil or mixtures thereof derived from the citrus fruit peel and an alkanoic acid of the formula R-COOH wherein R is a C_9 - C_{11} straight or branched alkyl group in an agronomically acceptable diluent carrier.

2. Synergistic composition for the control of ants, their larvae and eggs [Formicidae] containing as active ingredients an essential oil or mixtures thereof derived from the citrus fruit peel and an alkanoic acid of the formula R-COOH wherein R is a C_9 - C_{11} straight or branched alkyl group in an agronomically acceptable diluent carrier.

3. A synergistic composition according to claims 1 and 2 wherein said essential oil is selected from oils of the citrus fruit peel of orange, lemon and grapefruit or mixtures thereof.

4. A synergistic composition according to claims 1 to 3 wherein said essential oil is the orange fruit peel oil.

5. A synergistic composition according to claims 1 to 3 wherein said essential oil is lemon fruit peel oil.

6. A synergistic composition according to claims 1 to 3 wherein said essential oil is grapefruit peel oil.

7. A synergistic composition according to claims 3 to 6 wherein said carboxylic acid is capric acid.

8. A synergistic composition for the control of ants according to any of the previous claims and contains 0.1% to 5.0% by weight of said essential oil or mixture of said essential oils and 0.25% to 1.0% by weight of said carboxylic acid.

9. A synergistic composition according to claim 8 wherein said essential oil is orange fruit peel oil and contains 0.1% to 5.0% by weight of said oil and 0.25% to 1.0% by weight of capric acid.

10. A synergistic composition according to claim 8 wherein said essential oil is lemon fruit peel oil and contains 0.1% to 5.0% by weight of said oil and 0.25% to 1.0% by weight of capric acid.

11. A synergistic comp on according to claim 8 wherei id essential oil is grapefruit peel oil and contains 0.1% to 5.0% by weight of said oil and 0.25% to 1.0% by weight of capric acid.

12. A synergistic composition according to claim 8 wherein said mixture of said essential oils is selected from lemon peel oil, orange peel oil and grapefruit peel oil and 0.25% to 1.0% by weight of said carboxylic acid.

13. A synergistic composition according to claim 12 wherein said acid is capric acid.

14. A synergistic composition according to claims 12 and 13 wherein said mixture contains 0.1% to 5.0% by weight of said essential oils selected from lemon peel oil, orange peel oil and grapefruit peel oil.

15. A synergistic composition according to any of claims 1 to 14 in the form of liquids, emulsions, powders, wettable powders, suspensions, foams, pastes, granules or aerosols.

16. A synergistic composition according to any of claims 1 to 15 for combatting ants, their larvae or their eggs or any species of the Formicidae by applying said composition to the ants,their larvae or their eggs or any species of the Formicidae or to a habitat thereof.

17. A method of controlling ants,their larvae or their eggs, which comprises applying to said larvae or eggs an effective amount of the synergistic composition according to any of the preceeding claims.

18. A method of combatting ants,their larvae and their eggs, of the species *Tapinoma simrothi* according to claim 17.

19. A method of combatting ants,their larvae and their eggs of the species *Polyrhachis simplex* according to claim 17.

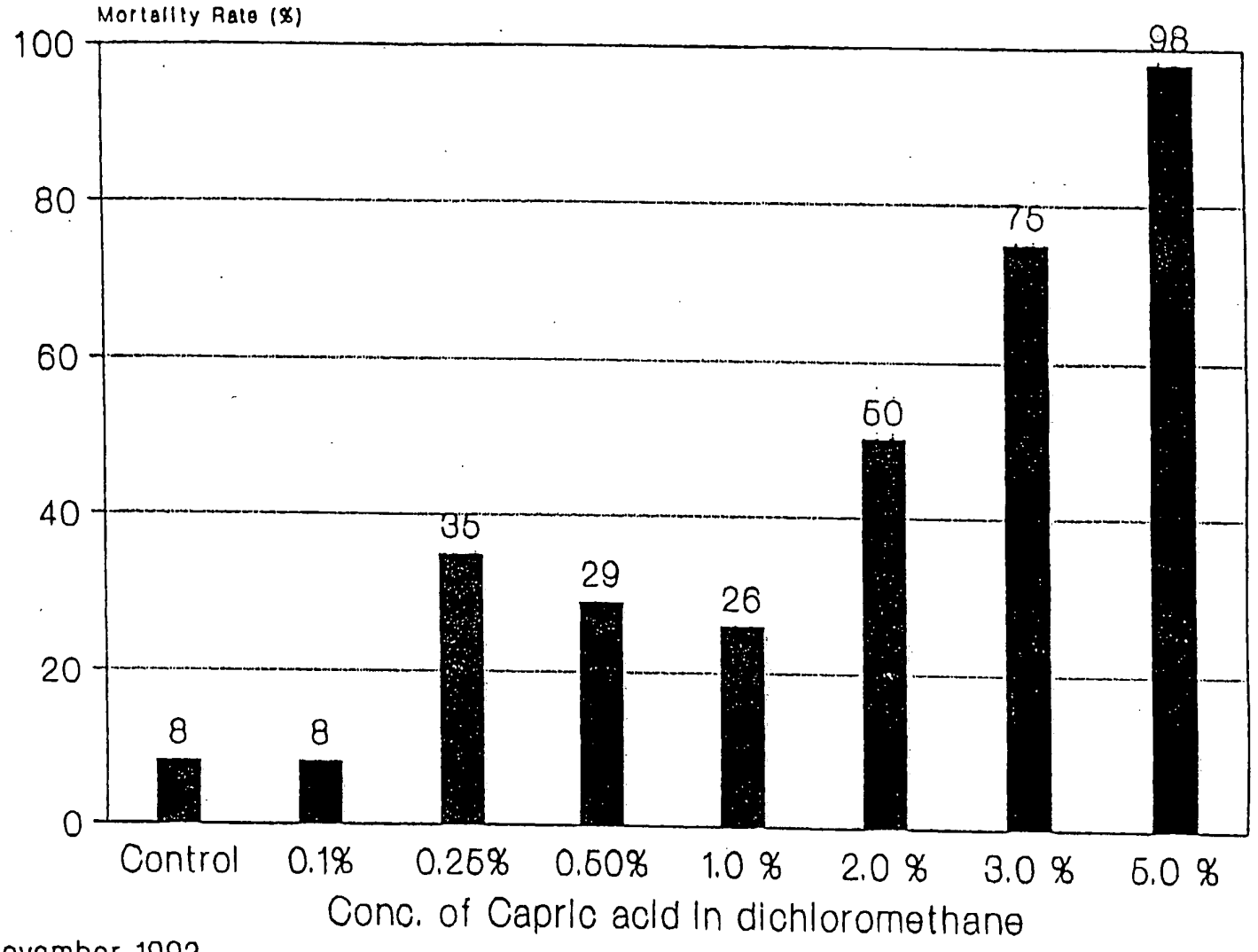
20. Use of the synergistic composition according to any of the claims 1 to 14, characterized in that the synergistic composition in the form of liquids, emulsions, powders,wettable powders, suspensions, foams, granules or aerosols are effectively applied to the area infected by ant, larvae or eggs.

Signature of Applicant J. Ofer

Dr. Yaacov Ofer

EFFECT OF CAPRIC ACID [C10] ON ANTS.

Tapinoma simrothi



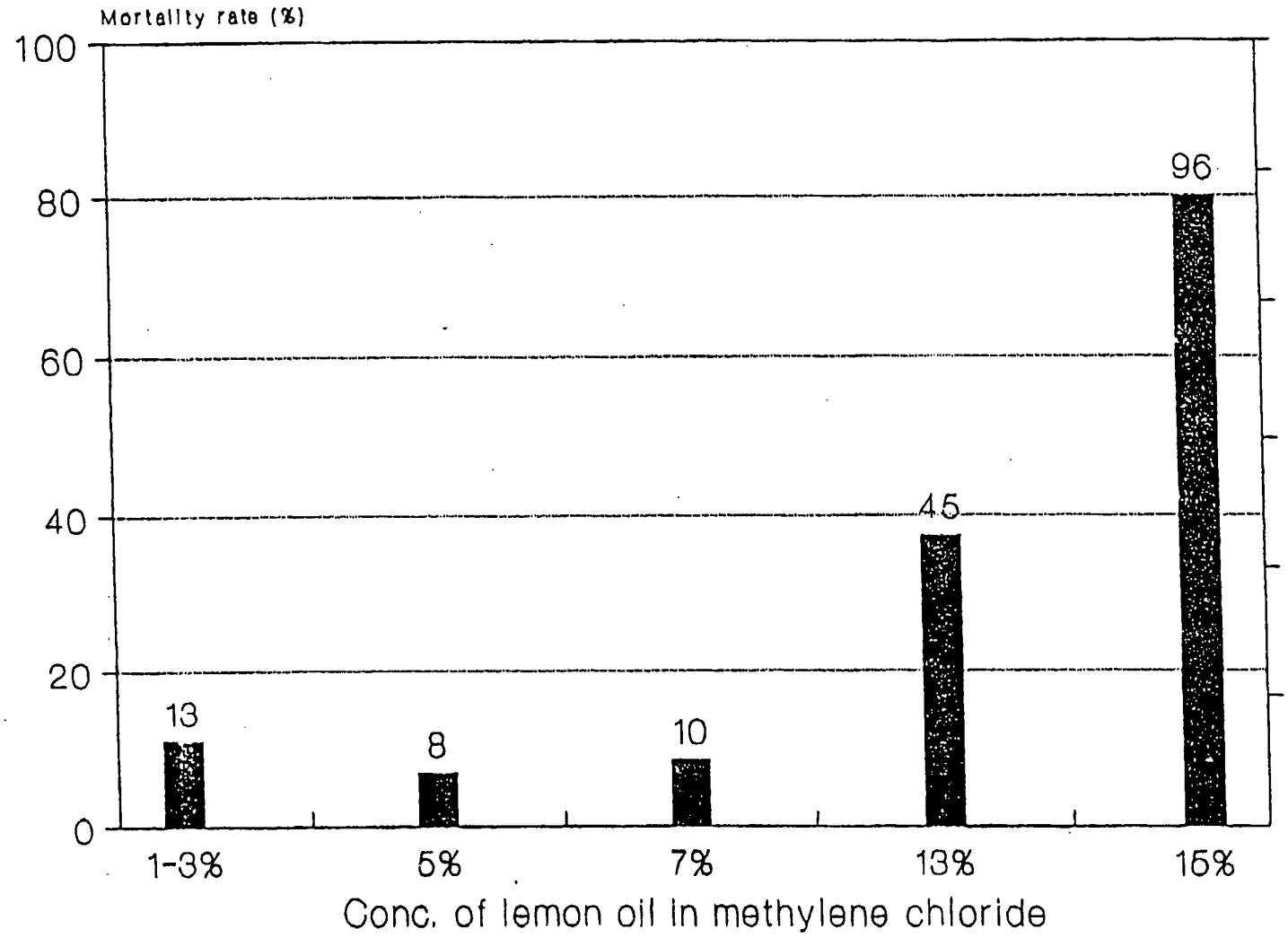
November 1992

Yaacov Ofra

FIGURE 1

Effect of Lemon Oil on ants.

Tapinoma simrothri



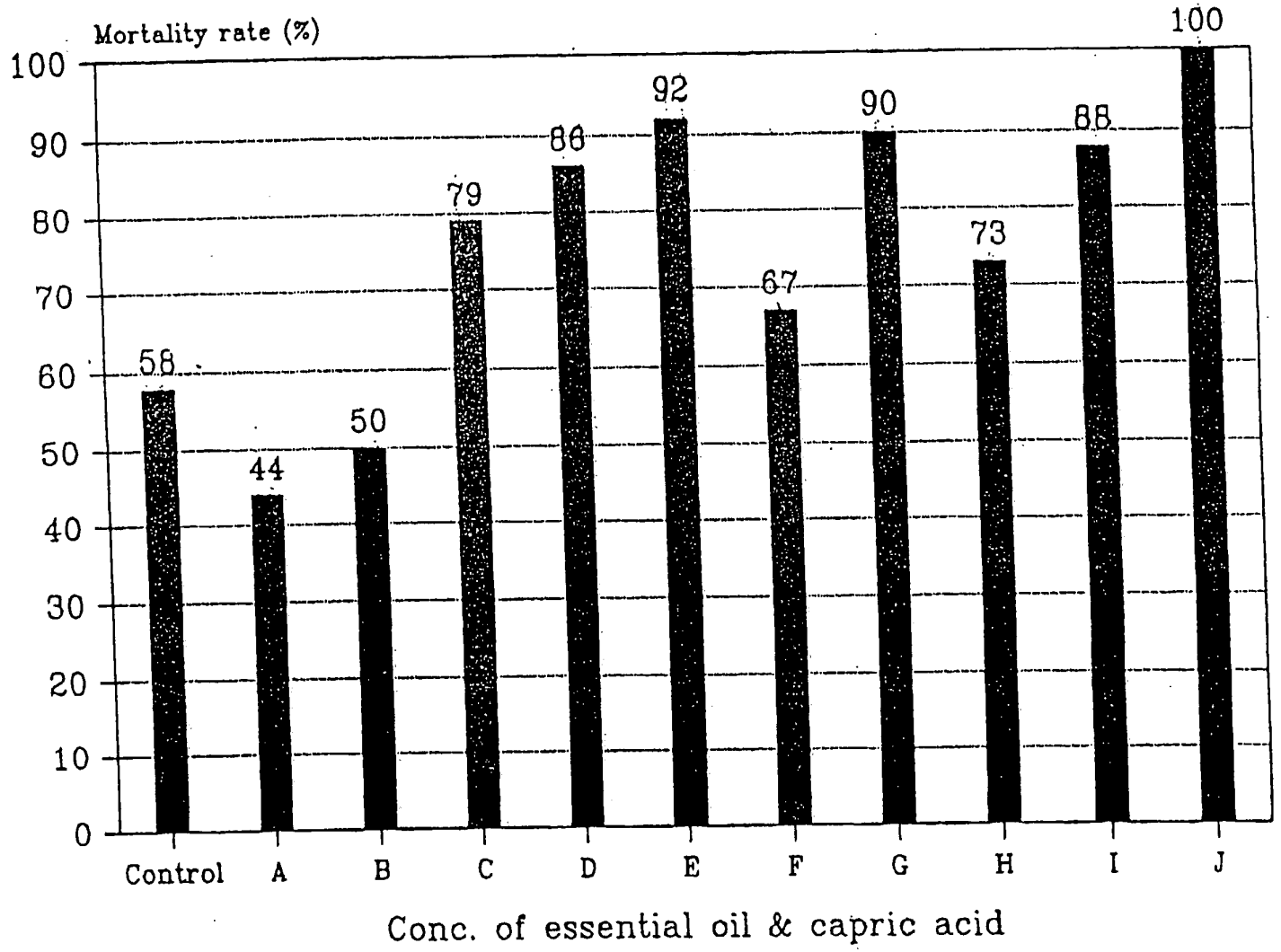
November 1992

Yaacov Ofer

FIGURE II

SYNERGISTIC COMPOSITIONS ON ANTS

Tapinoma simrothi



November 1992

Yaacov Ofir

EGGS & LARVAE OF WEAVER ANTS

Polyrhachis simplex

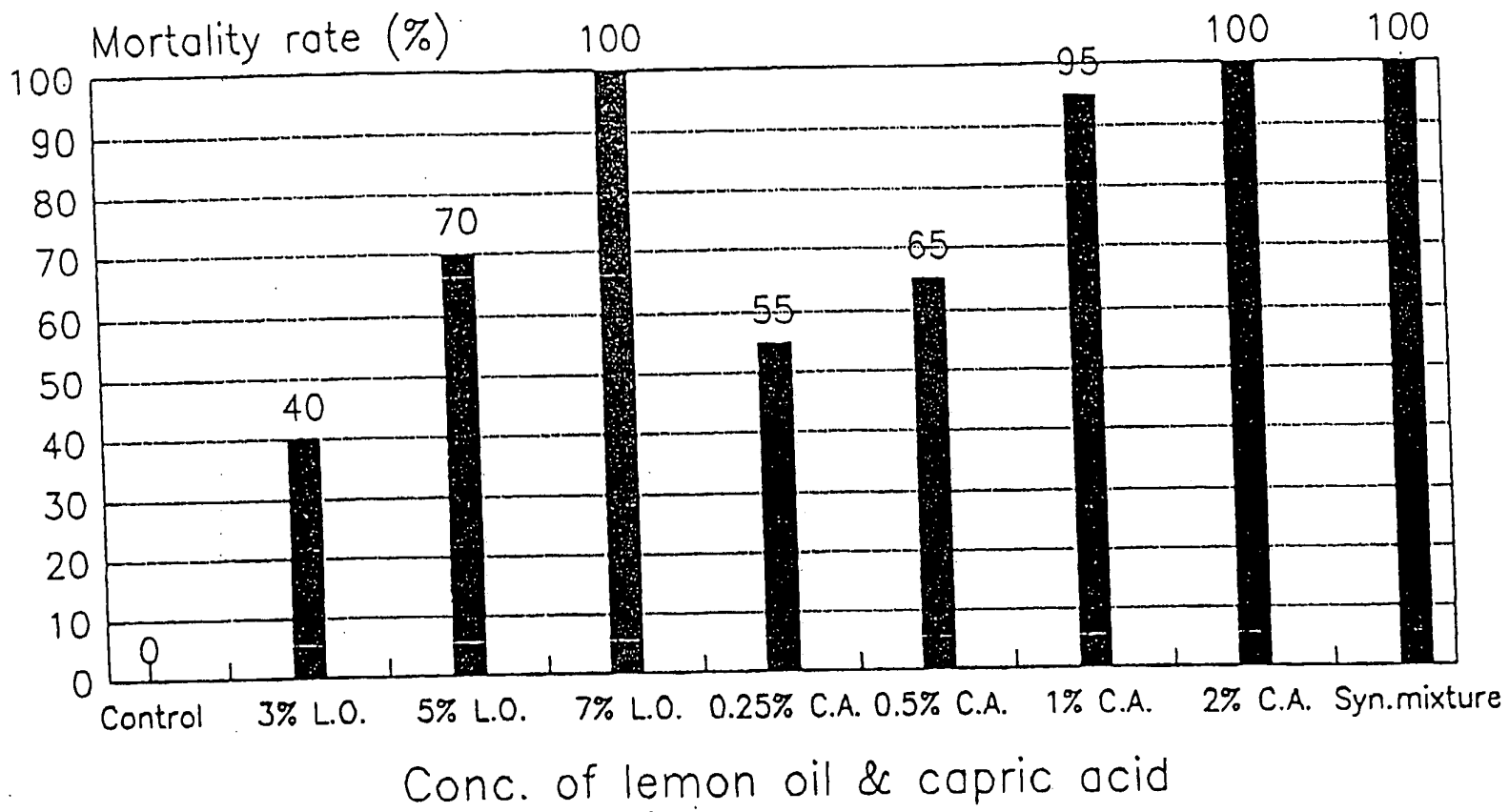


FIGURE IV

March 1993

Yaacov Ofer